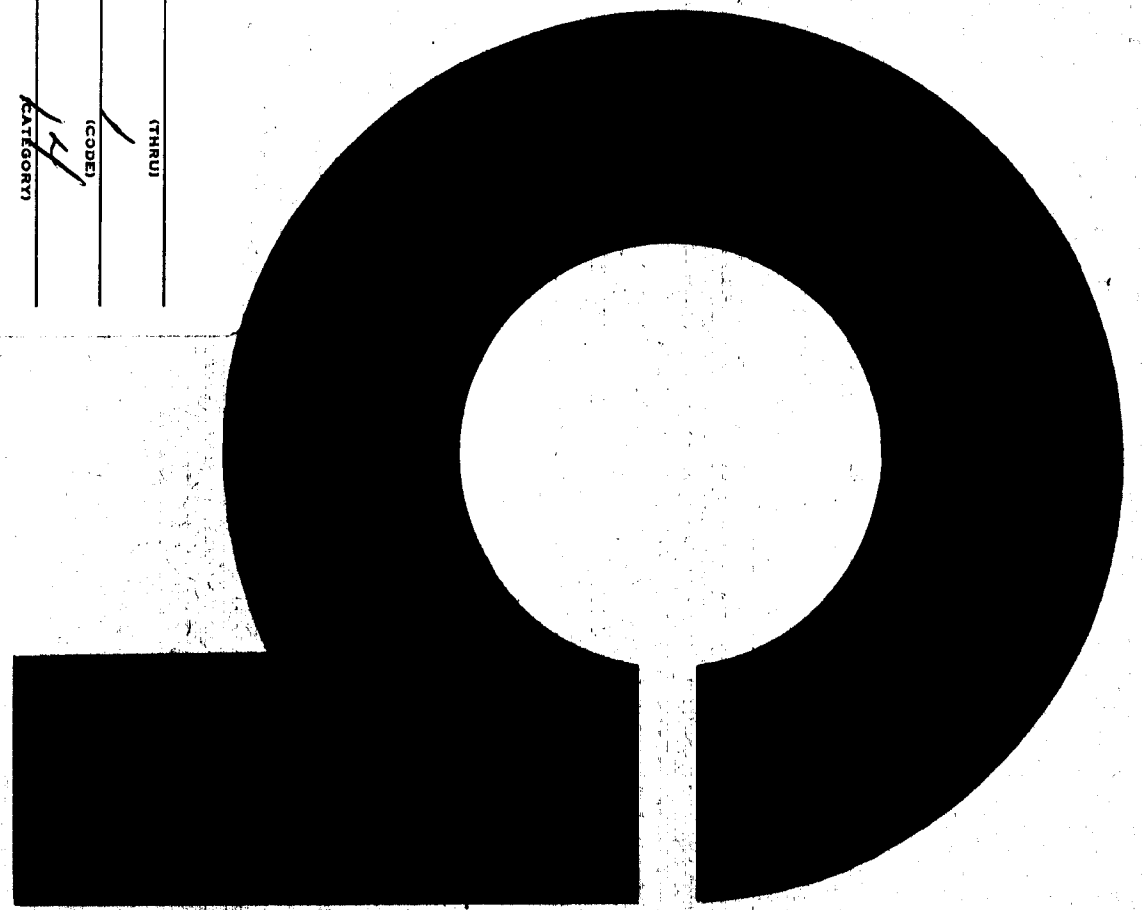

GEOPHYSICS CORPORATION OF AMERICA

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SOLIDS MASS SPECTROMETER

Fourth Quarterly Technical Progress Report

Contract No. NASw-839

SOLIDS MASS SPECTROMETER

N65-10819

During the fourth quarter of the contract period, a further significant reduction of the instrumental background was achieved by improved oil-free pumping of the duoplasmatron arc chamber and of the target chamber; impurities produced by the existing target holder were eliminated by replacing it with an adapter of spectroscopically pure tantalum.

The sensitivity of the instrument has been extended by improving the background and by installing a digital memory oscilloscope. In the case of boron-doped silicon, boron levels down to 47 parts per billion have been detected in this manner. Other tests on spectroscopically pure samples of graphite and platinum have also demonstrated the sensitivity and versatility of the instrument.

Author

I. BACKGROUND

As the sensitivity of the instrument is improved by refinements in experimental technique, additional sources contributing to instrumental background have been identified and eliminated.

(1) Duoplasmatron Arc Chamber

After prolonged operation of the duoplasmatron ion source, the purity of the primary argon beam deteriorated. This was manifested by the appearance of hydrocarbon peaks and of some mercury in the primary spectrum. Vacuum firing of the various ion-source electrodes resulted in only minor improvements.

Since the existing duoplasmatron arc chamber could be evacuated only via the beam exit hole, it was decided to add a manifold for differential pumping via an insulating section and a liquid-nitrogen trapped 2-inch mercury diffusion pump. In this manner, the argon flow through the arc chamber was increased by approximately a factor of 50, thus minimizing contamination from impurities within the ion source.

(2) Target Holder

The original target holder did not consist of spectroscopically pure tantalum. An adapter was constructed of spectroscopically pure material which is suitable for samples in rod form; it contained a known impurity level of 0.1% niobium which was readily detected with the instrument.

(3) Zeolite Roughing Pump on Target Chamber

In the system, as designed initially, the target chamber was evacuated via a by-pass line to the mechanical forepump. It was recognized that this might cause contamination of the target by forepump oil; as an intermediate precautionary measure, the target chamber was roughed directly from atmospheric pressure by cracking the isolation valve above the liquid-nitrogen trap of the main 6-inch mercury diffusion pump. Simultaneously with the modification of the arc chamber pumping system, a zeolite pump and isolation valve were added to the target chamber. The target chamber can now be evacuated from atmospheric pressure to the millitorr region in completely oil-free fashion.

The result of these changes is a greatly improved primary spectrum which, besides argon, contains only contributions due to water vapor, carbon monoxide and carbon dioxide, not exceeding 1 part in 10^4. The contribution of these mass peaks to the secondary spectrum is reduced further by several orders of magnitude.

II. SPECTRA OF SOLID SAMPLES

As stated in the previous quarterly report, the detection limit for trace impurities required a standard which, preferably, would consist of a mono-isotopic matrix and a single trace impurity with no possible overlap on the atomic mass scale. It was expected that meaningful data could be expected either from boron-doped silicon or from a mixture of selected impurity elements in spectroscopically pure graphite.

(1) Boron-doped Silicon

The spectrum of silicon includes the isotopic peaks of $Si^{+}(28,29,30)$, $Si^{2+}(14,14^{1/2},15)$ and $Si^{3+}(9^{1/3},9^{2/3},10)$. The spectrum of boron has its isotopic peaks at 10 and 11, the latter being the major peak. Considerable efforts have been made to obtain measurements of the B^{11} peak relative to the Si^{28} peak over a wide variety of samples. These were supplied, either in the form of solar cells, by the NASA, Goddard Space Flight Center (Dr. Fang) with the boron concentration varying as a function of depth from the surface, or, as homogeneous pellets, by the Dow-Corning Corporation, Hemlock, Michigan.

According to the Dow-Corning engineer, the impurity level in the crystals is determined by measuring the resistivity; this method is accurate up to 50 ppm. Above this concentration, errors by about a factor of 2 are possible.

It appears that there is, at present, no better standard below 1 part per million than the Dow-Corning samples. Preliminary results indicate that with these the detection limit of the solids mass spectrometer, using direct

readout, is about 20 parts per million of boron in silicon. However, using the integrating method described previously and storing the signal with the commercial digital memory oscilloscope, a further factor of improvement of approximately 1000 is obtained. The smallest concentration of boron in silicon measured to-date is 50 parts per billion, requiring a test period of about one hour.

Work on the solar cells has shown a large measurable change of the boron concentration in silicon with depth from the surface. However, the level of boron impurity indicated is larger than expected from manufacturing data (1 ppm) and further work is necessary to clarify this point.

(2) Spectroscopically Pure Graphite

This is the matrix of the material obtained from the Jarrell-Ash Company. As shown in the attached mass spectrum, the major contaminants are the alkali metals sodium and potassium, with traces of chromium, iron, copper, zinc and indium. Other peaks are atomic hydrogen and oxygen, argon from the primary beam, tantalum and mercury from the ion source and the vacuum system.

(3) Spectroscopically Pure Platinum

This sample was tested to confirm data obtained by emission spectroscopy, indicating that the total impurity level does not exceed one part per million and consists of Al, Si, Fe and Ag. Rather surprisingly, large peaks of Al, Ca and Zr were obtained, with subsidiary peaks of Ti, Cr, Fe. It is not clear, yet, why most of these contaminants have not been

detected by emission spectroscopy; however, it is interesting to note that crucibles of zirconium and aluminum oxides are used in the melting of platinum; these could be the origin of the contaminants detected.

It should be mentioned,that in the samples which have been analyzed before and after the platinum sample, these impurities do either not appear at all or with an intensity many orders of magnitude lower. It must, therefore, be concluded that these materials are really in the sample and not introduced by the instrument. The peaks of Al, Ca and Zr are so high that even 1/1000 of their intensity could easily be seen. If the spectroscopic analysis is correct that the concentration of these elements is much less than 1 ppm,then the solids mass spectrometer has a sensitivity much better than one part per billion for these particular elements in a platinum matrix. This seems to be a very favorable condition and it cannot be generalized that for all trace impurities this detection limit will be reached. More work is needed to gain a broader picture of the capabilities of the solids mass spectrometer for trace analysis.

APPENDIX

1. Primary beam spectrum after improvements of ion source and target chamber pumping.

2. Detection of 40 ppm boron in silicon (direct read-out).

3. Detection of 47 ppb boron in silicon (with digital memory oscilloscope).

4. Analysis of spectroscopically pure graphite.

5. Analysis of spectroscopically pure platinum.

PRIMARY BEAM

AS (7)

BUT

0.2A, 45°V

FILAMENT CURRENT MET ELSEWHERE

1x10^-7
1x10^-8
1x10^-9
1x10^-10
1x10^-11
1x10^-12

1×10^{-7} A

SILICON WITH 40 ppm BORON (DOW CORNING)

$^{29}Si / ^{28}Si = 0.047$

10KV A, 0.3A, 50V, 1×10^{-6} TORR

3000V MP

1100V ACC

LOG, $10^{10}\Omega$ SHUNT, 0 ... 10^{-7} A

1×10^{-8} A

1×10^{-9} A

1×10^{-10} A

1×10^{-11} A

1×10^{-12} A

H^+ Si^{++} $Si^{30}H^+$ $^{11}B^+$ $Si^{29}H^+$ O^+ $^{40}A^{++}$ $^{28}Si^+$ $^{29}Si^+$ $^{30}Si^+$ $^{40}A^+$ Si_2^+ Tc^+ Hg^+

SILICON WITH 47 ppb BORON (DOW CORNING)

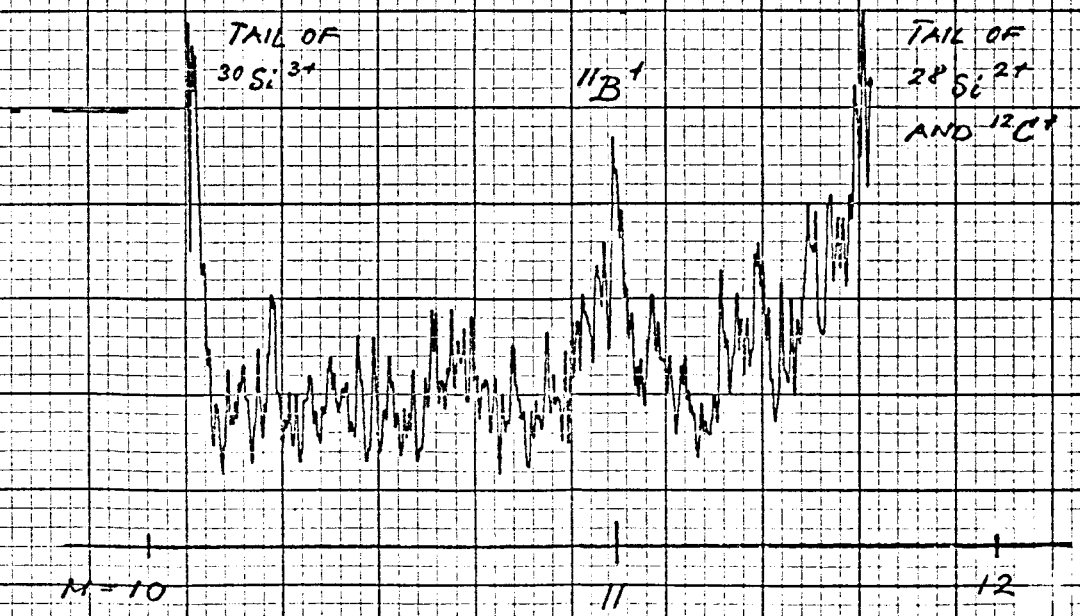
10KV A^+, 0.3A, 50V, 1×10^{-6} TORR

3500V MR
1000V ACC, 20% SWEEP

LIN, 100 mV, $10^{10}\Omega$, ENHANCE TRIM

SWEEPTIME 16 sec,

INTEGRATIONTIME 1 HOUR



PURE GRAPHITE

10 KV A^+, 0.28A, 45V, 1×10^{-6} TORR

3700 V MP

1000 V ACC

LOG, $10^{10}\Omega$ SHUNT 0,,, 10^{-7} A

1×10^{-7}

1×10^{-8}

1×10^{-9}

1×10^{-10}

1×10^{-11}

1×10^{-12}

$^{12}C^+$

$^{12}C_2^+$

$^{13}C^+$

CH_2^+

N^+

$^{41}A^+$

$^{12}(C\ ^{13}C)^+$

A^{2+}

Ne^+

$^{39}K^+$

$^{12}C_3^+$

CH_4^+

$^{16}O^+$

Cu^+

$^{41}K^+$

Cr^+

Fe^+

$^{13}C_3$

C_4^+

In^+

H^+

C^{2+}

A^{3+}

AL`Si

CC^+

Zn^+

Tl^+

Hg^+

PURE PLATINUM

10KV A^+, 0.28A, 50V, 1×10^{-6} TORR

3000V MP

1000V ACC

LOG, $10^{10}\Omega$ SHUNT 0... 10^{-7}

1×10^{-7}

1×10^{-8}

1×10^{-9}

1×10^{-10}

1×10^{-11}

1×10^{-12}

C_4^+ A^+

Ar^+

Zr^+

Ti^+

Pt^{2+}

Mo^+

Cr^+

Fe^+

Pt^{2+}

C^+ N^+ O^+ A^{2+}

B^+ Mg^+ Si^+ Ca^+ Ti^+ V^+ Mn Ga^+ Nb^+ Rh Hf^+ Ta^+ Pt^+